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Spatial Distribution and Decrease of Dye Solar Cell Performance Induced by Electrolyte Filling

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Abstract

The spatial performance variation of dye solar cell with standard liquid electrolyte was examined by dividing the cell into segments. Surprisingly large and permanent performance differences were found in different parts of the cell leading to significant losses in the overall cell efficiency. The decrease of open-circuit voltage along the electrolyte filling direction suggests that 4-*tert*-butylpyridine is adsorbed non-uniformly as the electrolyte passes through the dyed TiO₂ layer during the filling process. The result indicates that non-uniform electrolyte adsorption may limit the up-scaling of dye solar cells, which calls for the examination of electrolyte filling techniques and electrolyte compositions less prone to this effect.

Keywords: Dye-sensitized; Up-scaling; Spatial distribution; Electrolyte filling.

1. Introduction

Nanostructured dye solar cells (DSC) [1] have many advantages over the conventional solar cells such as simple manufacturing methods. The research of DSCs has developed to the point where the design of large area cell modules and even pilot production are current issues [2-5]. The large area solar cells have typically lower performance compared to small area cells [5-6]. One important reason for this are the problems in the current collecting in the large area cells.

In the upscaling of DSCs it is important that the performance is uniform throughout the cell. The spatial distribution of DSC performance has been examined previously in small scale using spatially resolved photocurrent imaging to study degradation [7-9].

The DSC modules are typically constructed of narrow and long cells, optimally about 1 cm wide [4]. In a serpentine design the total length of a single cell can be almost 2 m [5]. Here we focus on a stripelike cell which is divided into segments to study the spatial performance variation of photovoltaic characteristics. We find that the conventional electrolyte filling method can introduce spatial inhomogeneity on the DSC performance decreasing substantially the total cell efficiency.

2. Experimental methods

Traditional dye solar cells with fluorine-doped tin oxide (FTO) coated glass (2.5 mm, Pilkington TEC-15, sheet resistance 15 Ω /sq, Hartford Glass Company, Inc.) were studied here. Commercial titania paste (DSL 18NR-T, Dyesol) was used to prepare the TiO₂ films that were sintered at 450 °C for 30 minutes followed by 16 hours of sensitization in a dye solution consisting of 0.32 mM *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (Solaronix SA) in ethanol (99.5 wt-%). The resulting TiO₂ layer thickness was 15 μ m and the area of one segment TiO₂ film approximately 0.3 cm². The counter electrodes were thermally platinized

[10] at 385 °C for 15 min using 5 mM tetrachloroplatinate PtCl_4 (Sigma-Aldrich) dissolved in 2-propanol. The electrodes were attached together with either a 25 μm or 40 μm thick Surlyn[®] ionomer resin film spacer (DuPont) according to availability. Liquid electrolyte consisting of 0.5 M LiI, 0.03 or 0.05 M I_2 , and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile was inserted through filling channels drilled in the substrate. The electrolyte with the lower I_2 concentration was used with the thinner spacer film to establish same limiting current in all cells. Only cells with similar spacer and electrolyte are compared in the Figures and Tables. More detailed specifications of the cell components and preparation are shown elsewhere [12]. The cell structure was not optimized for high performance.

The conductive FTO layer of the substrates was divided into electrically isolated segments (Figure 1). In addition to 4-segment cells, 2-segment cells such as previously used for internal reference electrode studies were prepared [13]. The segment cells are compared with simultaneously prepared small single cells having the same geometry and size of the dyed TiO_2 layer as in the individual segment. The segment nearest to the electrolyte filling hole is referred to as Segment 1 and the other segments are numbered consecutively towards the other end (Figure 1).

Photovoltaic measurements were performed on a black platform using a solar simulator providing 1000 W/m^2 AM1.5G equivalent light intensity determined by a calibrated silicon reference cell with spectral filters to mimic typical DSC response. The polarization curves were measured using a Keithley 2420 SourceMeter[®]. The 2-segment cells and their reference single cells were provided with black masks with a slightly larger aperture size compared to the active area since it results in the most reliable results [14].

3. Results and discussion

A cell in which the active area was divided into two identical segments showed clear spatial difference in the photovoltaic parameters (Table 1). In Segment 1, which was near the electrolyte filling hole, the open circuit voltage V_{OC} was approximately 100 mV larger compared to Segment 2 (Table 1). The short circuit current density i_{SC} was approximately 2 mA/cm² larger in Segment 2 than in Segment 1. While the higher i_{SC} and V_{OC} values of the two segments were rather similar to those of the single cells, both segments had lower efficiency than the single cell as indicated in Table 1. More importantly, the total efficiency of the segmented cell was lower than that of the average efficiency in each segment (Table 1).

As the two segments in the 2-segment cells were geometrically identical, there were differences neither in optics nor in the amount of electrolyte surrounding the photoactive area. The only asymmetry was introduced by the electrolyte filling in which the electrolyte in Segment 2 had passed through Segment 1 in the filling process. To investigate this issue directly, 2-segment cells with electrolyte filling hole between the segments were prepared. In these symmetrically filled cells the photovoltaic performance was equal in both segments and corresponded to that of the single cells, proving that the spatial performance variation in Table 1 is due to the electrolyte filling process.

Consistently with this dividing a longer cell into four segments induced similar performance variation: V_{OC} was again highest and i_{SC} lowest in the segment nearest to the electrolyte filling hole, and V_{OC} decreased systematically towards the end of the cell (Figure 2). i_{SC} was in turn highest in the middle segments (Figure 2). The efficiency of the four segments connected in parallel gave approximately 20 % lower efficiency compared to a small single cell.

The decrease of V_{OC} along the electrolyte filling direction suggests that some electrolyte component that increases the V_{OC} is rapidly adsorbed (filtrated) into the dyed TiO_2 layer as it passes through and over it. 4-*tert*-butylpyridine (4-tBP), which is a common additive in DSC electrolytes, is known to increase V_{OC} by suppressing recombination [15]. 4-tBP has also been shown to decrease i_{SC} which is considered to be caused by a shift in the conduction band levels of the TiO_2 with respect to the excited state of the dye, which also contributes to higher V_{OC} [16-17]. Indeed, when using electrolyte with no 4-tBP in it, the photovoltaic parameters in the segments of 2-segment cells were similar except for a very small difference in V_{OC} : the average V_{OC} in Segment 1 was (0.414 ± 0.005) V and in Segment 2 (0.397 ± 0.002) V. In case of 4-segment cells without 4-tBP the different ends of the cells gave similar V_{OC} : average V_{OC} in Segment 1 (0.37 ± 0.01) V and in Segment 4 (0.36 ± 0.01) V. Interestingly enough, the middle cells gave about 20 mV lower V_{OC} compared to the segments in the end: V_{OC} in Segment 2 (0.35 ± 0.01) V and in Segment 3 (0.34 ± 0.01) V. While relatively small, this difference between the end and the middle cells might be due to their different geometric location which results in small differences in optics and in the amount of electrolyte surrounding the photoelectrode (cf. 2-segment cells in which this does not occur). These results give strong indication that the observed performance variations in the cells with 4-tBP are mainly due to spatial distribution in the amount of adsorbed 4-tBP in the dyed TiO_2 film.

In the 4-segment cells without 4-tBP i_{SC} decreased steadily from Segment 1 to Segment 4 by approximately 10 %. This decrease may be due to the same reason that caused the lower i_{SC} in Segment 4 in 4-segment cells with 4-tBP. The reason for this spatial difference remains unclear.

To study whether the differences are permanent, the segmented cells were aged over a period of 15 days in the dark at room temperature. The photovoltaic characteristics of the different segments varied over time (Figure 3), but the difference between the segments was permanent. In fact, the

difference in i_{SC} even grew (Figure 3B). Intriguingly, Segment 1 had larger statistical deviation of performance compared to Segment 2 (Figure 3). The reason for this remained unclear.

With the active area of 1.2 cm^2 in the 4-segment cell, the unevenness of the performance led to cell efficiency loss of 20 %. It is unclear how much this loss would increase if the cell area was increased further. In some studies showing comparison of small cell and module data the performance differences have been smaller [2,4-5]. However, in those studies the active area of the small cells has been about twice as large as here [2,4-5]. It is therefore possible that the losses caused by the spatial variation are already saturated in relatively small cell size. The spatial variances caused by the filling process are affected by the hydraulic conductivity which depends for instance cell geometry. In addition, the effect of 4-tBP depends largely on the other components in the electrolyte [17].

4. Conclusions

Dividing the dye solar cell into electrically separated segments revealed clear spatial performance variation in the cell. The effect was permanent and could be linked to uneven distribution of 4-*tert*-butylpyridine, a commonly used additive. As a result, the overall efficiency of the segmented cell was 20 % lower than a small single cell.

The results indicate that the conventional electrolyte filling method can introduce uneven distribution of adsorbed electrolyte species affecting the cell performance. To reach high performance in large area cells, advanced electrolyte filling techniques such as screen or inkjet printing could be considered to reach a more uniform electrolyte distribution. Alternatively, an evenly distributing electrolyte could be designed.

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Captions

Table 1. The average performance characteristics and their standard deviations (three cells) for different segments of 2-segment cell and their calculated parallel connection in comparison with single cells.

Figure 1. The structure of the 4-segment cell. The dashed lines indicate the gaps in the conductive layer of the substrate.

Figure 2. Typical IV data of different segments in 4-segment cell (continuous lines) and the measured parallel connection (dashed line). The segment number descends in proportion to V_{OC} as indicated in the figure.

Figure 3. Average A) V_{OC} and B) i_{SC} data of three 2-segment cells as a function of time t . The errorbars indicate the standard deviation and they are plotted when larger than the marker size.